Quality Issues Regarding the Watercourses from Middle Basin of Jiu River

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The study aims to characterize the quality of surface waters in the middle of the river basin Jiu by monitoring physicochemical indicators of their quality, in 2013-2015. In this regard, the pH, dissolved oxygen (DO), biochemical oxygen demand (BOD_5) of nitrate (NO_3^-), nitrite (NO_2^-), ammonium (NH_4^+), total phosphorus (P_{total}), chlorides and sulphates from water have been determined. Water of Jiu River and its tributaries of Gorj county have been monitored on representative sections for the evolution of their quality. It was found that the water from natural reservoirs monitored shows an evolution in the limits permitted by the regulations in force except biochemical oxygen demand and nitrites indicators for river Jiu and Tismana and nitrate and chloride content for Gilort River.

Keywords: watercourses, quality indicators, monitoring

One of the fundamental resource for human well-being and the natural environment is freshwater being regarded as the most essential natural resource in the world [1].

Due to the interactions hydrosphere - atmosphere - the lithosphere - living organisms, chemical composition and quality of natural waters are in constant change. Biological, chemical and physical processes that modelling water ecosystem are very complex. The chemical composition of natural waters are varied under different conditions [2]. They contain a large number of substances, namely: dissolved gases coming mainly from the atmosphere with the water is in contact or from chemical reactions that occur in water, organic or inorganic matter (plant debris, microorganisms, mineral dust, sand, etc.), various amounts of dissolved salts [3-7]. Rains wash particulate matter at the water-air interface, and they introduced them in surface waters. The atmosphere contains water vapor in a concentration which varies with temperature and pressure. The content of water vapor in the atmosphere is estimated by the air humidity that is opposed to the diffusion of pollutants and their concentrations decrease, preventing the particles movement. High humidity leads to the formation of fog that produce concentration of impurities.

At lithosphere-water interface, dissolving minerals and rocks by water depends on several factors such as the nature of rocks and minerals, the (grain size and porosity rocks), contact time and temperature. Some minerals are dissolved in water without the intervention of chemical reactions, such as alkali chlorides, limestone, gypsum, etc., and other are dissolved as a result of more complex processes such as hydrolysis, hydration, oxidation-reduction, the activity of microorganisms [8]. Chemical and biochemical reactions at the water-lithosphere interface adjust the composition of natural waters. Minerals and rocks play an essential role in storing and immobilization of chemical species, such as heavy metals, but also their reinsertion into the water cycle, according to a number of conditions regarding the *p*H and redox potential.

It can be say that surface waters are the most exposed to the risks of different types of pollution. In case of violent rains, whashes waters and torrents travel and transport all kinds of materials that change the chemical composition of water. In addition, anthropic activities are known to be the most important water pollution sources. In most cases, the wastewater from the tanning industry, paper, sugar, dyes, mining, chemical, are discharged directly into rivers without any prior treatment [9]. The diversity and complexity of the sources of pollution causes significant changes in the chemistry of natural waters, their quality and usability in various fields [10,11]. Therefore, monitoring of water quality is a complicated problem [12].

Experimental part

Assessment of watercourses monitored between 2013-2015, in terms of the evolution of their quality was done by sampling of the river Jiu. This river is considered dominant for Gorj county hydrography. There were also monitored two major tributaries such as Gilort and Tismana Rivers, which are located in the middle of the river basin Jiu. Sampling methods used were those provided by current water quality standards. New polyethylene containers have been used for this purpose to reduce the possibility of contamination. Sampling vessels were completely filled with water and tightly closed during immersion to prevent oxidative processes at oxygen-water interface [13]. Sections of monitoring and sampling points were established based on the inventory of sources of pollution of watercourses monitored. In Gorj county, a major influence on the quality of natural waters have discharges of untreated or insufficiently treated wastewater from municipal and industrial activities.

Analyzes were performed to determine some physico-chemical indicators of surface water such as pH, dissolved oxygen (DO), biochemical oxygen demand (BOD_5), nitrates (NO_3^-), nitrite (NO_2^-), ammonium (NH_4^+), phosphorus total (P_{total}), chloride, sulphate. Analytical methods applied were those standardized namely: water *p*H was measured potentiometric using a pH meter portable model Hanna [14], the content of nitrates [16], nitrites [18], ammonia [17] and total phosphorus [19] was determined by spectrophotometric methods using a UV spectrophotometer -VIS T70. The chlorides [20], dissolved oxygen [15] and biochemical oxygen were determined by

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Table 1
PHYSICO-CHEMICAL INDICATORS FOR JIU RIVER (2013-2015)

Monitored indicators	JIU RIVER S1- upstream of Sadu confluence; S2- downstream of Tg. Jiu; S3 – upstream of Tismana confluence								
	2013			2014			2015		
	S1	S2	S3	S1	S2	S3	S1	S2	S3
pH	7.42	7.42	7.72	7.14	7.33	7.44	7.59	7.67	7.57
Nitrate (mg/L)	0.79	0.94	0.9	0.91	0.89	0.84	0.86	0.93	0.87
Nitrite (mg/L)	0.023	0.035	0.025	0.028	0.027	0.024	0.038	0.041	0.021
Ammonium (mg/L)	0.06	0.09	0.06	0.08	0.15	0.13	0.06	0.07	0.06
Total phosphorus (mg/L)	0.08	0.05	0.07	0.06	0.07	0.08	0.12	0.09	0.14
Dissolved oxygen(mg/L)	10.9	9.67	10.4	10.58	10.25	10.14	10.96	10.64	11.68
BOD_5 (mg/L)	3.2	3.4	2.8	3.4	3.6	2.5	3.2	3.8	2.7
Chloride (mg/L)	12.05	15.7	16.54	14.98	13.87	12.82	6.68	8.72	11.87
Sulphate (mg/L)	19.6	18.77	22.12	19.39	19.67	17.32	18.20	18.45	16.45

volumetric methods and the sulphate content was determined by the colorimetric method using model Orbeco-Hellige photometer.

Results and discussions

The values recorded for watercourses analyzed were reported to the value of maximum limit concentrations in accordance with Norm 161/2006 concerning the classification of surface waters in order to determine the ecological status of water bodies [21].

Table 1 shows the average values of physical and chemical indicators of quality of Jiu river, monitored in three sections: upstream of Sadu confluence, downstream of Tg. Jiu and upstream of Tismana confluence in 2013-2015.

Graphical representations of indicators measured and reported to the maximum permissible values according to norm 161/2006 submitted for quality class I for Jiu River, are shown in figures 1-4.

The results of analysis performed for Jiu River indicate that *p*H values are within the limit value (LV) of water quality standards (*p*H 6.5-8.5) ranging between 7.42 – 7.72 *p*H units. The average dissolved oxygen content is between 9.67 and 11.68 mgO_2/L. According to these values, Jiu River water can be classified as I Class Quality water under Order 161/16 February 2006 (LV for DO = 9 mg O_2/L). The average content of NO_3^- is below the limit values for I Class Quality water under Order 161/16 February 2006 (LV for NO_3^- = 1 mg N/L). The value for

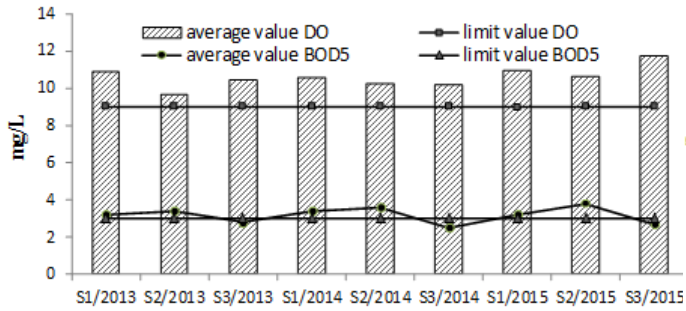

Fig.1. Dissolved oxygen and BOD_5 concentration values for Jiu River

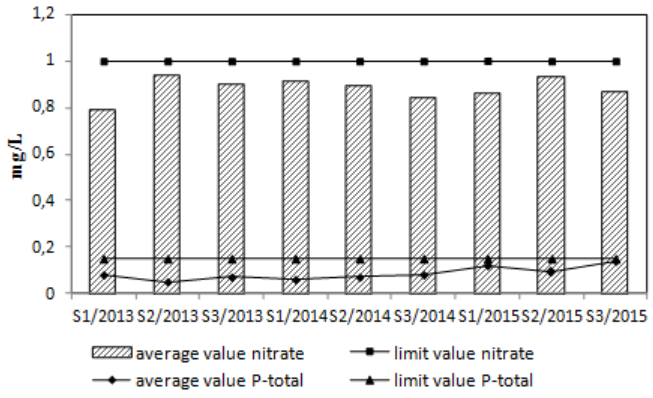

Fig 2. Nitrate and Total Phosphorus average concentration

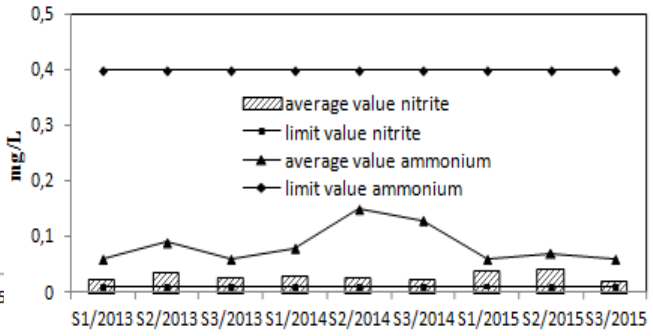

Fig 3. Nitrite and Ammonium average concentration values for Jiu River

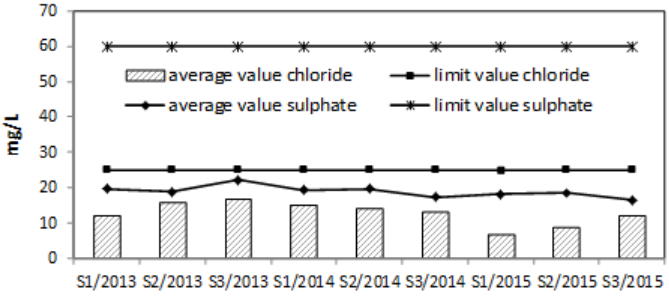

Fig. 4. Chloride and Sulphate average concentration values for Jiu River

Monitored indicators	Tismana River Monitoring S1- upstream of Tismanita confluence; S2- Calnic;					
	2013		2014		2015	
	S1	S2	S1	S2	S1	S2
pH	7.18	7.26	7.30	7.49	7.20	7.28
Nitrate (mg/L)	0.45	0.69	0.44	0.45	0.40	0.44
Nitrite (mg/L)	<0.002	0.016	0.002	0.008	<0.002	0.006
Ammonium (mg/L)	0.021	0.063	0.023	0.034	0.021	0.022
Total phosphorus (mg/L)	0.06	0.08	0.06	0.05	0.12	0.13
Dissolved oxygen(mg/L)	10.80	10.45	10.71	9.76	12.26	12.28
BOD_5 (mg/L)	2.5	2.6	2.5	2.8	3.1	3.4
Chloride (mg/L)	14.59	17.53	14.86	11.44	16.27	17.64
Sulphate (mg/L)	21.05	22.21	21.36	21.75	21.70	24.29

Table 2
PHYSICO-CHEMICAL INDICATORS FOR TISMANA RIVER (2013-2015)

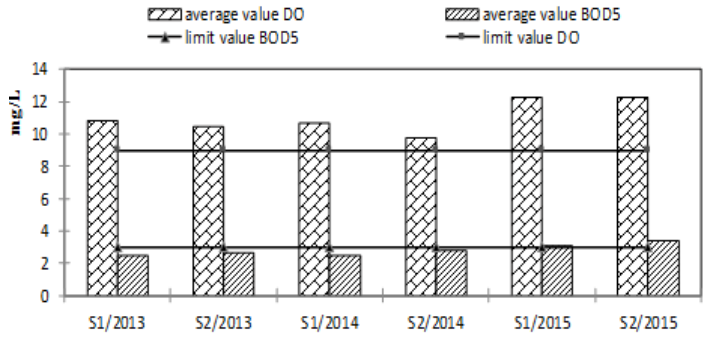

Fig. 5. DO and BOD_5 concentration values for Tismana River

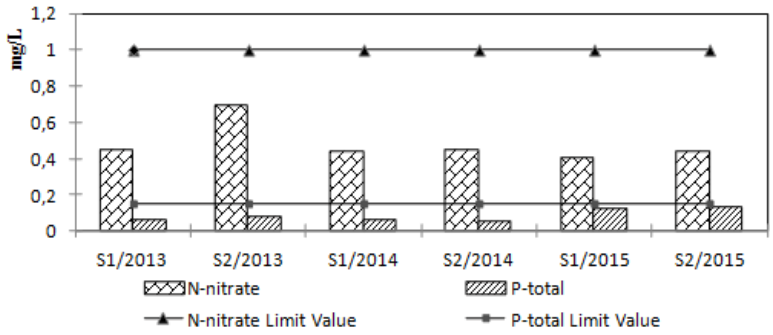

Fig. 6. Nitrate and Total Phosphorus concentration values for Tismana River

biochemical oxygen demand exceeds the limit value for for first class quality (under 161/2006 Norm BOD_5 = 3 mg O_2/L) for two of the three monitored sectors, namely upstream and downstream of the confluence Sadu Tg. Jiu, indicating a pollution by of Jiu River with organic substances most likely due to insufficiently treated wastewater discharged into the environment. Exceedings are between 1.07 LV (limit value) for the section S1 and 1.26 LV (limit value) for the section S2. The average of nitrite content recorded for the Jiu River exceeded the Class I quality limit (LV = 0.01 mgN/L) for all monitored sections. It may be noted that the recorded values are in the range of 4.1 LV to 2.1 LV for nitrate content, the higher value corresponds to section S2 (downstream Tg. Jiu), in 2015. The total phosphorus content is between 0.05-0.14 mgP/L which is below the limit of 0.15 mgP/L, while the chloride and sulphate content are below the limit value for first class quality (the limit for Cl^- is 25 mg/ L, and for sulphate limit value is 60 mg/L).

Table 2 shows the average values of quality indicators for Tismana River, a right tributary of the middle river basin Jiu recorded in 2013-2015. Sampling was performed in two sections: upstream of confluence Tismanita and Calnic.

Graphical representation of indicators monitored in the period 2013-2015 for the two sections of the Tismana River and them reporting them to the maximum permissible norm are shown in figures 5-7 under 161/2006 Norm.

The values of Tismana River indicators measured (fig. 5-7) and reporting them to maximum permitted levels indicate the following conclusions: pH values are in the range 7.18 to 7.49 units. *p*H and average dissolved oxygen content is above the limit value for quality Class I being between 9.76 to 12.28 mg O_2/L. It was observed an exceedance of the limit value for biochemical oxygen demand in 2015, in section S2 (Calnic) of 1.13LV (limit value). In the same year, in section S1 (upstream of Tismanita confluence) the average value of BOD_5 LV

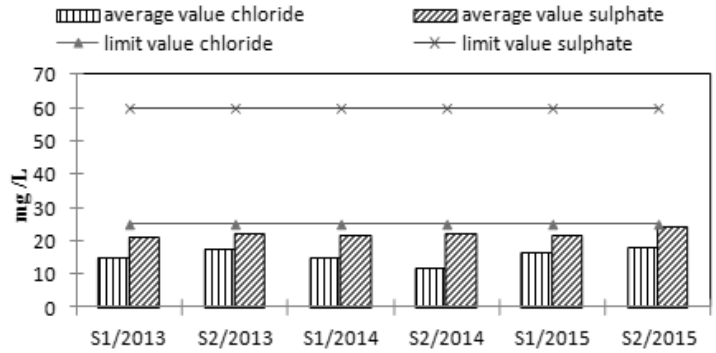

Fig. 7. Chloride and sulphate concentration values for Tismana River

Table 3

PHYSICO-CHEMICAL INDICATORS FOR GILORT RIVER (2013-2015)

Monitored indicators	Gilort River Monitoring S1- Turburea; S2- Bengesti; S3 – upstream of Novaci								
	2013			2014			2015		
	S1	S2	S3	S1	S2	S3	S1	S2	S3
pH	7.72	7.48	7.56	7.66	7.34	7.43	7.38	7.44	7.31
Nitrate (mg/L)	0.78	0.49	0.35	0.59	0.37	0.31	0.71	0.31	0.26
Nitrite (mg/L)	0.019	<0.002	<0.002	0.031	<0.002	<0.002	0.043	<0.002	<0.002
Ammonium (mg/L)	0.103	0.029	<0.018	0.070	0.022	<0.018	0.044	<0.018	< 0.018
Total phosphorus (mg/L)	0.09	0.08	0.07	0.07	0.06	0.09	0.07	0.02	0.04
Dissolved oxygen(mg/L)	9.97	10.70	10.90	11.59	10.75	11.05	12.03	12.31	12.86
BOD_5 (mg/L)	2.3	2.6	2.8	2.5	1.9	1.7	2.8	2.7	2.3
Chloride (mg/L)	35.38	17.79	15.22	27.86	23.80	26.66	36.87	26.76	24.25
Sulphate (mg/L)	32.37	21.63	26.93	27.87	24.94	22.66	34.62	25.7	21.95

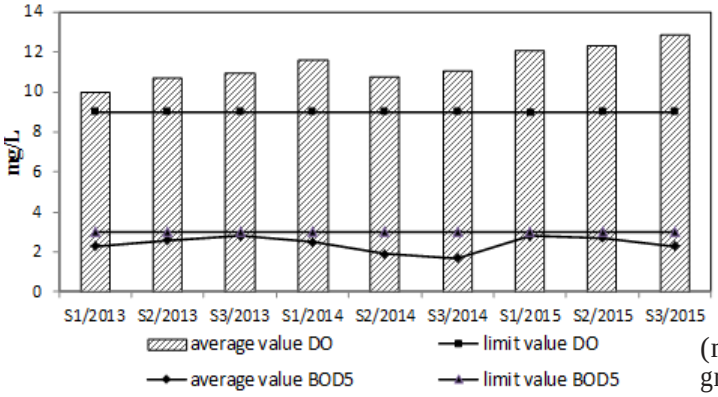

Fig. 8. DO and BOD_5 concentration values for Gilort River

is 1.07, which indicates an average pollution of the river Tismana in these secions with organic compounds.

For the monitored period, the average content of nitrates was the range 0.40 to 0.69 mgN/L, total phosphorus values were between 0.05 to 0.13 mgP/L, chloride content between 11.44 - 17.64 mg/L and the sulfates varied between 21.05 and 24.29 mg/L. All these values are below the limit value for first class quality water.

Table 3 presents the average values of the physico-chemical quality indicators for Gilort River, a left tributary river of the river basin Jiu monitored in 2013-2015 in three areas sampling: Turburea, Bengesti and upstream of Novaci.

Physico-chemical indicators measured for samples of river Gilort were also reported to Norm 161/2006 (maximum allowable values for quality class I). Their graphical evolution is shown in figures 8-10.

It was found that for Gilort River, the *p*H values are within the limits allowed by Norm 161/2006, the average dissolved oxygen content is between 9.97 to 12.86 mg O_2/L being higher than the limit value for I Quality Class and average values for BOD_5 are below the permissible limit (BOD_5 LV = 3 mg O_2/L). Regarding the nutrient regime expressed by the nitrate content, it was observed that this corresponds to I Quality Class for Gilort River. The nitrite content exceeds the limit of I Quality Class for section S1 being in the range 1.9LV - 4.3 LV. The total phosphorus content is between 0.02 to 0.09 mgP/L, these values are below the limit of 0.15 mgP/L.

In case of Gilort River, it was found exceedings of chloride content values. The maximum permitted level for I Quality Class is 25 mg/L. Average concentrations

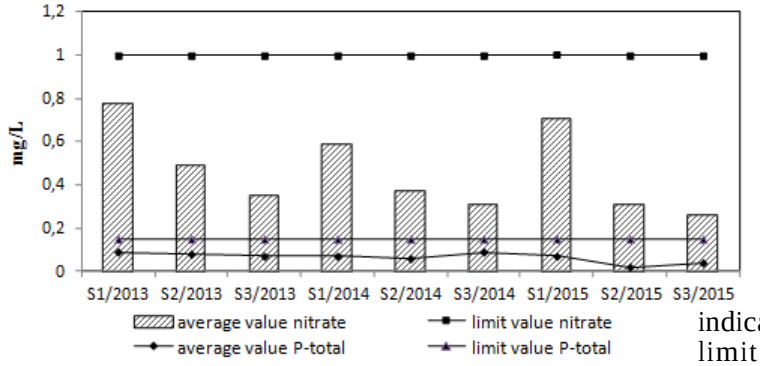

Fig. 9. Nitrate and Total Phosphorus concentration values for Gilort River

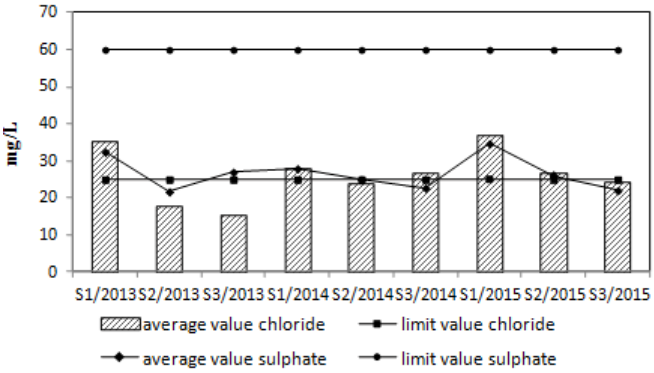

Fig. 10. Chloride and sulphate concentration values for Gilort River

of chlorides registered during 2013-2015 in section S1 (Turburea) were between 1.14 LV and 1.47 LV which indicates a degree of environmental pollution due to human activities with chlorides in the Gilort River. It was found that there were no exceedings of of the limit value for I Quality Class (SO_4^{2-} = 60 mg/L).

Conclusions

The aim of this work was to characterize the evolution of the quality of water courses in the catchment area of the river Jiu by monitoring physicochemical indicators of Jiu river and its main tributaries, Tismana and Gilort. In this respect, during 2013-2015, was conducted sampling of representative sections of the rivers analyzed. Monitoring of quality indicators: *p*H, nitrates, nitrites, ammonium, total phosphorus, dissolved oxygen, biochemical oxygen, chlorides and sulfates allowed the evaluation of the quality of watercourses in study, by comparing the measured values to the values indicated in Norm 161/2006 .

By analysing the Jiu River recorded data indicates its affiliation I Water Quality Class regarding the indicators monitored, with the exception of biochemical oxygen demand. Average levels for this indicator reveals Jiu River pollution by organic substances due to domestic and industrial wastewater insufficiently treated discharged into the environment. The average nutrient content recorded for the Jiu river exceeds also the limit of the I Water Quality Class for all monitored sections. The higher values for nutrient content were recorded for downstream of Tg. Jiu.

Tismana river monitoring was conducted in two areas of monitoring for 2013-2015. Tismana River indicators measured were reported to the limit values mentioned in the Normative 161/2006. There were found exceedings of the limit value for biochemical oxygen demand in 2015, which indicates an average organic pollution of the river Tismana. For the period monitored, the average content of nitrite, nitrate, total phosphorus, chloride and sulphate are below the limit value for I Water Quality Class.

The average values of physical and chemical indicators of Gilort River monitored during 2013-2015 indicated an average dissolved oxygen higher than the limit value for I Class Quality. Nutrients regime expressed by nitrate and total phosphorus is below the limit value for I Class Quality, but the nitrate content exceeds the limit value for one of the monitored sections. For Gilort River, it was found chloride content values over the limit quality corresponding to I Class Quality which means an average pollution of Gilort River due to industrial activities from particular area.

Consequently, from this study it can be concluded that monitoring of water courses plays an important role in understanding and predicting of anthropogenic and natural impacts of pollution sources offering an important tools for managing the natural ecosystems.

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